UNIVERSITI PUTRA MALAYSIA

PHYSICO-CHEMICAL PROPERTIES AND OXYGEN SPECIES BEHAVIOR OF BULK AND MODIFIED VANADIUM PHOSPHATE CATALYST FOR PARTIAL OXIDATION OF *N*-BUTANE

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By

TANG WEN JIUNN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

August 2008

Special Dedication to My Beloved Family

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

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Chairman: Professor Taufiq Yap Yun Hin, PhD, CChem, MRSC (UK)

Faculty: Science

Vanadium phosphate catalyst is well known for the selective oxidation of *n*-butane to maleic anhydride process. In this study, the behavior of oxygen species in vanadium phosphate catalysts was investigated using temperature programmed analyses. Besides, the effects of Mo and Te dopants addition and mechanochemical treatment also have been studied. A new method to synthesis $VOPO_4 \cdot 2H_2O$ using milling technique (mechanosynthesis) also included in the study. The catalysts were synthesized by calcining the precursor, $VOHPO_4 \cdot 0.5H_2O$ in a flow of *n*-butane in air (0.75% *n*-butane in air) for 16 h at 733 K. Precursor was obtained by reduction of $VOPO_4 \cdot 2H_2O$ using *iso*-butyl alcohol. The physico-chemical properties of the catalysts were characterized by using x-ray diffraction (XRD), BET surface area measurement, redox titration, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM) and temperature programmed analyses. The catalytic properties of the selected catalysts were carried out by using temperature programmed reaction (TPRn) and on-line microreactor system. A comparison between the fresh and used catalysts in aerobic and anaerobic condition gave the better understanding about the lattice oxygen species which took

part in the selective oxidation. It was found that, certain amount of O^{2-} species which associated with V^{5+} plays an important role in selectivity for maleic anhydride because no O^{2-} species was detected by temperature programmed reduction (H_2-TPR) for the used catalyst in anaerobic condition. This result also supported by TPRn profile for the post O_2-desorbed catalyst where the catalyst with only O^- species gave no significant selectivity compared to catalyst with both oxygen species (O^{2-} and O^-). However, deleterious effect was observed for catalysts with high number of V^{5+} species (catalysts from mechanochemically treated doped precursors). High amount of O^{2-} species was obtained by H_2-TPR for these catalysts. However, this oxygen species only promotes total oxidation as only CO_2 was observed in *n*-butane oxidation. Introduction of Mo and Te into the catalyst precursor did not change the phase of the final catalysts. However the doped catalysts consist only platelets particles and no rosette clusters morphology as usually observed for dihydrate route catalyst. Mechanochemical treatment on the doped precursors did not change the $VOHPO_4{\cdot}0.5H_2O$ phase of the precursors but increased the number of β-$VOPO_4$ in the catalysts stage. Besides that, the surface area reduced significantly and the morphology also changed from platelets to blocky shape. According to the TPRn results, all the catalysts from the doped precursor gave higher conversion compared to undoped counterpart. However, the catalysts from mechanichemically treated doped precursors have low selectivity because no intermediate products were observed. A new method of $VOPO_4{\cdot}2H_2O$ preparation was successfully carried out using mechanosynthesis method. The product synthesized ($VOPO_4{\cdot}2H_2O$) in 2 h at 1400 rpm using agate materials has lower crystallinity compared to the refluxed counterpart. The surface area for the catalyst produced from the mechanosynthesized $VOPO_4{\cdot}2H_2O$ was slightly lower than conventional catalyst but increased after the

precursor was mechanochemically treated prior calcination step. Meanwhile, the total oxygen removed for the catalysts from mechanosynthesized $VOPO_4 \cdot 2H_2O$ was lower compared to conventional catalyst.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SIFAT-SIFAT FIZIKAL-KIMIA DAN KELAKUAN SPESIS OXIGEN DALAM PEMANGKIN VANADIUM FOSFAT GUMPALAN DAN DIMODIFIKASI UNTUK PENGOKSIDAAN SEPARA *N*-BUTANE

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Mangkin vanadium fosfat terkenal dengan process pengoksidaan terpilih *n*-butana kepada maleik anhidrida. Dalam kajian ini, sifat-sifat spesis oksigen dalam mangkin vanadium fosfat telah dikaji menggunakan analisis suhu terprogram. Selain itu, kesan-kesan daripada dopan Mo dan Te serta rawatan mekanokimia turut dikaji. Kaedah baru dalam sintesis $VOPO_4 \cdot 2H_2O$ dengan menggunakan teknik kisaran (mekanosintesis) juga disertakan dalam kajian ini. Mangkin-mangkin telah disintesis dengan mengkalsinkan prekurser, $VOHPO_4 \cdot 0.5H_2O$ dalam aliran *n*-butana dalam udara (0.75 % *n*-butana dalam udara) selama 16 j pada 733 K. Prekurser disintesis dengan menurunkan $VOPO_4 \cdot 2H_2O$ menggunakan alkohol *iso*-butil. Sifat-sifat fizikal-kimia mangkin telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), pengukuran luas permukaan BET, pentitratan redox, plasma gandingan teraruh-spektoskopi pancaran atom (ICP-AES), mikroskopi electron imbasan (SEM) dan analysis-analysis suhu terprogram. Sifat pemangkinan untuk mangkin terpilih telah dijalankan dengan menggunakan reaksi suhu terprogram (TPRn) dan sistem rektor mikro on-line. Perbandingan di antara mangkin segar dan mangkin terpakai dalam keadaan aerobik dan anaerobik memberikan pemahaman yang lebih baik berkenaan

spesis oksigen kekisi yang memainkan peranan dalam pengoksidaan terpilih. Didapati bahawa sejumlah spesis O^{2-} yang dikaitkan dengan V^{5+} memainkan peranan penting dalam selektiviti kepada maleik anhidrida kerana tiada spesis O^{2-} dikesan oleh penurunan suhu terprogram (H_2-TPR) untuk mangkin terpakai dalam keadaan anaerobik. Keputusan ini disokong oleh profil TPRn untuk mangkin selepas penyahjerapan-O_2 di mana mangkin yang mempunyai spesis O^- memberikan selektiviti yang tidak siknifikan berbanding dengan mangkin yang mempunyai kedua-dua spesis oksigen (O^{2-} and O^-). Walaubagaimanapun, kesan buruk telah diperhatikan untuk mangkin dengan jumlah spesis V^{5+} yang tinggi (mangkin dari prekurser didop yang dirawat secara mekanokimia). Amaun spesis O^{2-} yang tinggi didapati oleh H_2-TPR untuk mangkin-mangkin tersebut. Walaubagaimanapun, spesis oksigen ini mempromosikan pengoksidaan lengkap di mana hanya CO_2 diperhatikan dalam pengoksidaan *n*-butana. Pengenalan Mo dan Te ke dalam prekurser mangkin tidak mengubah fasa pada mangkin. Walaubagaimanpun, mangkin-mangkin yang didop hanya mengandungi partikel kepingan dan tiada morfoloji kluster ros yang selalu diperhatikan untuk mangkin dari laluan dihidrat. Rawatan mekanokimia pada prekurser yang didop tidak mengubah fasa $VOHPO_4{\cdot}2H_2O$ prekurser tetapi menambahkan bilangan β-$VOPO_4$ dalam peringkat mangkin. Selain itu, luas permukaan berkurangan secara siknifikan dan morfologi juga berubah dari kepingan ke bentuk blok. Menurut keputusan TPRn, semua mangkin dari prekurser didop mempunyai penukaran yang lebih tinggi berbanding mangkin yang tidak didop. Walaubagaimanapun, mangkin-mangkin dari prekurser didop dirawat secara mekanokimia mempunyai selektiviti yang rendah kerana tiada produk pertengahan yang dikesan. Kaedah baru penghasilan $VOPO_4{\cdot}2H_2O$ telah berjaya dilaksanakan dengan menggunakan kaedah mekanosintesis. Produk ($VOPO_4{\cdot}2H_2O$) disintesis

dalam 2 j pada 1400 ppm menggunakan bahan agate mempunyai tahap kristal yang rendah berbanding yang direfluks. Luas permukaan mangkin dari $VOPO_4 \cdot 2H_2O$ mekanosistesis kurang sedikit berbanding mangkin konvensional tetapi meningkat selepas prekurser dirawat secara mekanokimia sebelum langkah pengkalsinan. Semetara itu, jumlah oksigen yang dikeluarkan dari mangkin dari $VOPO_4 \cdot 2H_2O$ mekanosintesis lebih rendah berbanding mangkin konvensional.

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I certify that an Examination Committee has met on 15th August 2008 to conduct the final examination of Tang Wen Jiunn on his Doctor of Philosophy thesis entitled "Physico-Chemical Properties and Oxygen Species Behavior Of Bulk and Modified Vanadium Phosphate Catalyst for Partial Oxidation Of *n*-Butane" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree of Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of Supervisory Committee were as follows:

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Date: 13 November 2008

DECLARATION

I declare that the thesis is my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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TANG WEN JIUNN

Date:

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LIST OF ABBRIVIATIONS

BET	Brunauer Emmer Teller
FWHM	Full-Width at Half Maximum
GHSV	Glass Hourly Space Velocity
H_2-TPR	Temperature Programmed Reduction in Hydrogen
$I_{(020)}/I_{(204)}$	Intensity ratio of (020) and (204) reflection planes
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standard
Mo/V	Molybdenum/Vanadium
MS	Mass Spectrometer
m/z	Mass to charge ratio
O_2-TPD	Temperature Programmed Desorption of Oxygen
P/V	Phosphorus/Vanadium
rpm	Round per minute
SEM	Scanning Electron Microscopy
TAP	Temporal Analysis of Products
TCD	Thermal Conductivity Detector
Te/V	Tellurium/Vanadium
TPRn	Temperature Programmed Reaction
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Catalysis in General

In general, catalyst is a substance that increases the rate of a reaction (Atkins and Paula, 2002). It happens by introducing new pathways with lower Gibbs activation energy, ΔG as shown in Figure 1.1. Although the activation energy is much lower than the uncatalyzed reaction, the Gibbs energy of overall reaction, $\Delta G^{\ominus}$ remain the same (Shriver and Atkins, 2001). It is important that the product is released in a thermodynamically favorable step.

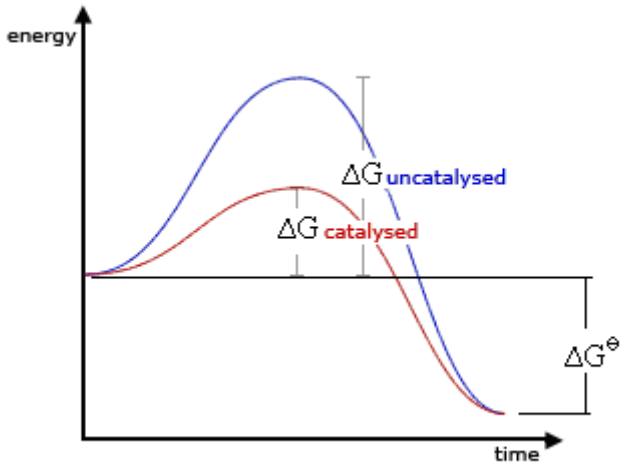

Figure 1.1. Schematic representation of the activation energy between catalyzed and uncatalyzed reaction (Shriver and Atkins, 2001)

A good catalyst should has three important criteria (Shriver and Atkins, 2001 and Atkins and Paula, 2002):

i) Activity

An active catalyst should has a strong chemisorption ability in order to attract reactant. However if it is too strong, the activity declines either because other reactants cannot react with the adsorbate or because the adsorbate molecules block the active sites thus prevent further reaction.

ii) Selectivity

A selective catalyst should produce high percentage of desire product with minimum amount of side products. It is economically important because highly selective catalyst reduce the consumption of reactants thus reduce the operation cost.

iii) Life time

A catalyst must survive through a large number of cycles. However, side reactions or presence of impurities in the reactants might deactivate the catalyst.

1.2 Selective Heterogeneous Oxidation Catalysis

Selective heterogeneous oxidation catalysis is playing an important role to the well being of society since it produces about 25% of the most important industrial organic chemicals and intermediates such as acrolein, maleic anhydride, ethylene and phthalic anhydride to be used in the manufacture of industrial products and consumer

goods (Grasselli, 2002). A desirable selective oxidation process must produce the desired products in high selectivity and high yield. This is a challenging task where the desired products are produced instead of carbon monoxide or dioxide, which are total combustion products and are thermodynamically more favorable (Kung, 1986).

1.2.1 Types of Selective Oxidation Reactions

Selective oxidation reaction can be classified into two types:

i) Oxidative dehydrogenation

ii) Partial oxidation

1.2.1.1 Oxidative Dehydrogenation

Dehydrogenation is a process in which a hydrocarbon molecule is converted into a more unsaturated hydrocarbon by breaking C-H bonds and forming C=C bonds (Kung, 1986). Catalytic dehydrogenation is introduced to convert paraffins to olefins. However the yields are low and there are some limitations (Centi *et al.*, 2001 and Nieto, 2006):

i) Deactivation of catalyst by coke formation.

ii) High operation temperature (973-1073 K) depends on paraffin.

iii) Difficulties to separate alkenes from alkanes and by-products.

As the solution to the above problems, oxidative dehydrogenation was introduced. The advantages of oxidative dehydrogenation are (Centi *et al.*, 2001 and Nieto, 2006):

i) Formation of water which overcome thermodynamically limitation.